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"Polynuclear Hydrocarbons"

R.W.Rimmer B.Sc.

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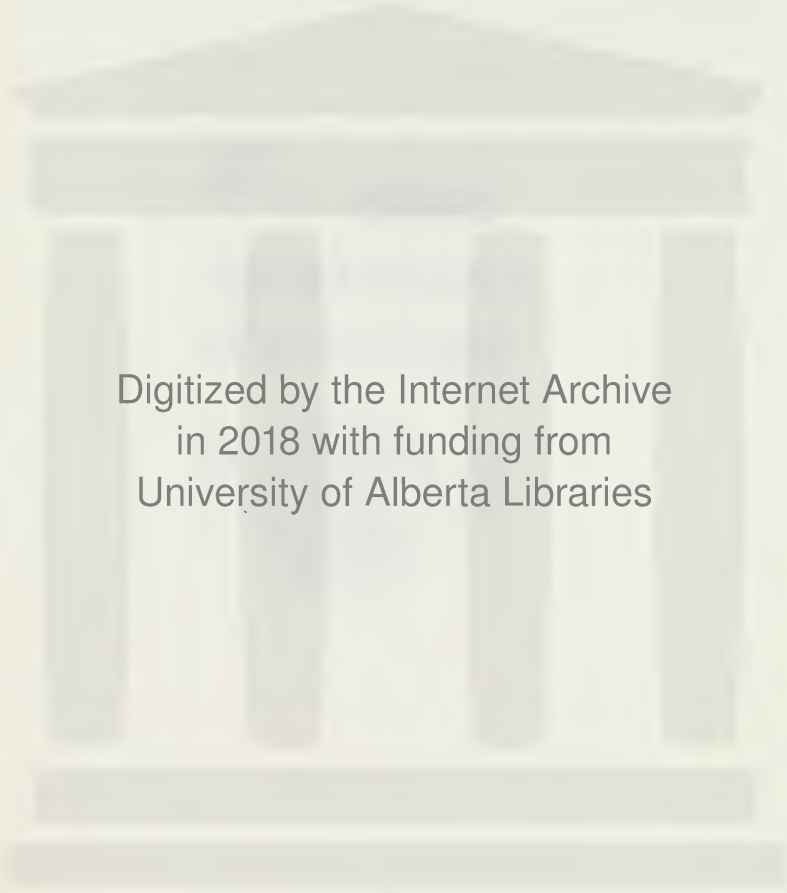
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A Thesis

by

R. W. Rimmer B. Sc.

University of Alberta

Department of Chemistry

April 1948

Polynuclear Hydrocarbons

Submitted in Partial Fulfilment

of the

Requirements for the degree of

Master of Science

by

R.W.Rimmer B.Sc.

Under the direction of

Dr.R.B.Sandin

Time devoted to this work....16 months

Edmonton, Alberta April 1948

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The author wishes to express his sincere appreciation to all who have assisted in the completion of this work.

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Introduction

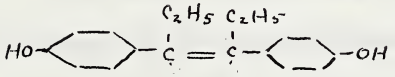
Introduction

The work reported herein is concerned primarily with the syntheses of compounds related structurally to diethylstilbestrol and dimethylstilbestrol. In addition to this mention will be made regarding the synthesis of 9,10-dialkylanthracene and related compounds.

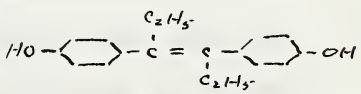
Diethylstilbestrol is a very interesting and powerful physiologically active substance. It was first made from desoxyanisoin by Dodds, Goldberg, Lawson, and Robinson (1). It exhibits estrous-exciting properties equal to those of estradiol and estrone and it is now known to be capable of inducing breast and testis tumors in mice of susceptible strains (2).

Diethylstilbestrol is used to produce a marked dormancy in cell mitosis of cancer of the prostate.

Stilbestrol can exist in two geometrical isomeric forms:



cis

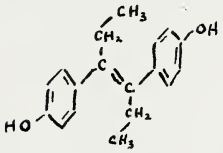


trans

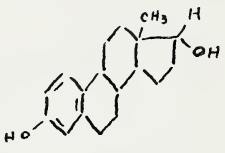
Yours truly,

Enclosure

The cis isomer has only a fraction of the activity of the trans isomer which can be expected by comparing the structure of trans stilbestrol with that of the powerful estrogen estradiol.

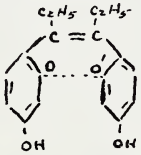


trans stilbestrol



estradiol

If the o,o' positions in stilbestrol are joined, the resulting compound is 3,6-dihydroxy-9,10-diethylphenanthrene.



The latter compound may be interesting due to the fact that 9-ethylphenanthrene has been found to exhibit estrogenic action. (3)

For that reason the preparation of 3,6-dihydroxy-9,10-diethylphenanthrene has been the main topic of this research. Although up to date this synthesis has not actually been accomplished

much has been learned which will be of help in the synthesis. A compound which is very similar in structure and which has been synthesized is 3,6-dimethoxy-9,10-dimethylphenanthrene.

The Synthesis of some 9,10-Dialkylphenanthrene and 9,10-Dialkylanthracene Compounds

For the ultimate synthesis of 3,6-dimethoxy-9,10-dialkylphenanthrenes it was necessary to first establish some route to the preparation of the simpler 9,10-dialkylphenanthrenes.

Some of the latter compounds have been synthesized by Bradsher(4) using his aromatic cyclodehydration method. Zincke and Tropp(5) tried to prepare these compounds by reducing the corresponding 9,10-dialkyl-9,10-dihydrophenanthrene-diols with red phosphorus and hydrogen iodide. They succeeded in preparing the 9,10-dimethylphenanthrene but there is some doubt as to whether or not they obtained the 9,10-diethylphenanthrene. Also it is possible that under the conditions they used for their experiments hydrogen iodide would attack methoxy groups. Thus the reduction method of Zincke and Tropp could not be used in the synthesis of dimethoxy-dialkylphenanthrenes.

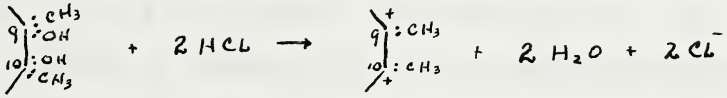
Conant (6) has prepared free radicals from triaryl carbinols using reducing agents such as titanous and vanadous salts in the presence of mineral acids.

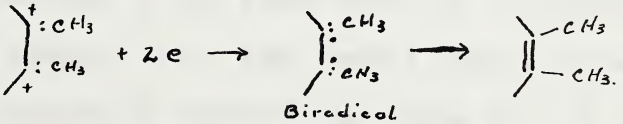
$$R_3C\text{-}OH + HX \rightarrow H_2O + R_3C^+X^-$$

$$R_3C^+ + V^{++} \longrightarrow R_3C\cdot + V^{+++}$$

Since no vanadous or titanous salts were available stannous chloride and concentrated hydrochloric acid was used. The mechanism of the reaction might involve the formation of the salt followed by reduction to a biradical which would result in the formation of the 9,10-dialkyl hydrocarbon.

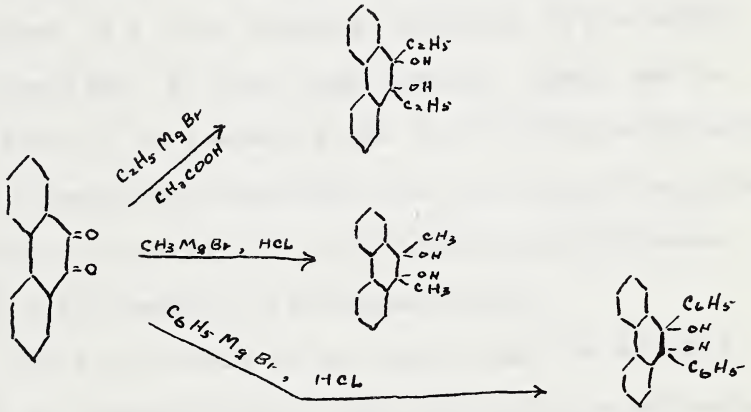
Let us then consider carbon atoms nine and ten in a molecule of 9,10-dimethyl-9,10-dihydrophenanthrene-diol.



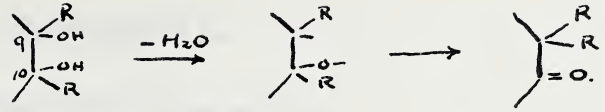


The two free electrons in the biradical pair off to form the second bond between the carbon atoms nine and ten.

Three diols, 9,10-dimethyl-9,10-dihydrophenanthrene-diol, 9,10-diethylphenanthrene-diol, and 9,10-diphenylphenanthrene-diol were made from phenanthraquinone and the appropriate Grignard reagent.



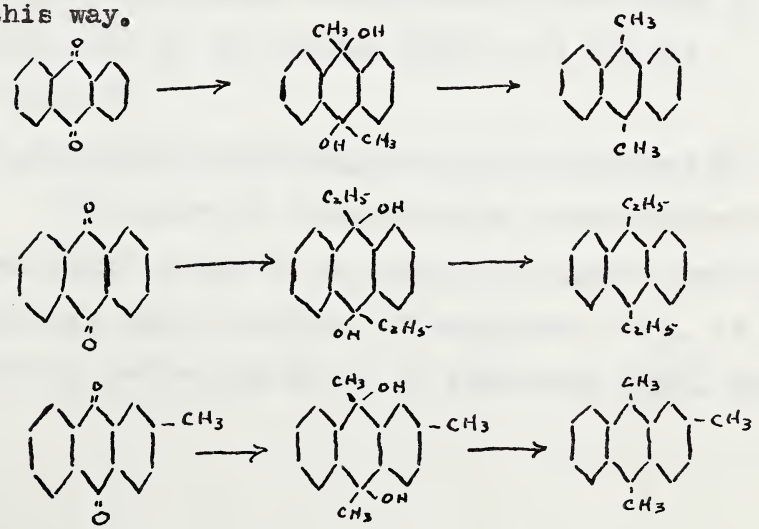
The reduction of each diol with stannous chloride and concentrated hydrochloric acid was tried. Only in the case of the dimethyl-diol was the reduction a success and 9,10-dimethylphenanthrene was obtained. With the other two diols rearrangement occurred and it was found that for 9,10-phenanthrene-diols groups larger than methyl groups migrate in the presence of concentrated acids to give substituted phenanthrones.



Similarly it was found that anthraquinone, when treated in a like fashion, afforded 9,10-dialkyl derivatives. In this case however, there was no difficulty in preparing the 9,10-diethylanthracene.

β-methylanthraquinone and 1,2-benzanthraquinone yielded respectively 2,9,10-trimethylanthracene and 9,10-dimethyl-1,2-benzanthracene

This procedure is one that could be adopted for the preparation of any 9,10-dialkylanthracene but only 9,10-dimethylphenanthrenes can be made this way.



Experimental.

Phenanthraquinone (7).

To a hot mixture of 250 cc. of concentrated sulfuric acid, 750 cc. of water in a 3-l. beaker was added 50 g. of crude phenanthrene. Potassium dichromate (150 g.) was then slowly added and the mixture was stirred for one hour. After diluting the product to a volume of two litres, the crude quinone was collected and washed. The products from two such reactions were united and reoxidized using 650 cc. of water, 250 cc. of sulfuric acid and 175 g. of potassium dichromate.

The crude product was purified by two recrystallizations from glacial acetic acid. A 57% yield of the quinone melting at 205° was obtained.

9,10-Dimethyl-9,10-dihydrophenanthrene-diol (8).

Five grams of finely divided phenanthraquinone was added slowly to an ice-cold Grignard reaction mixture made from 1.8g. of magnesium, 10 g. of methyl iodide and 50 cc. of anhydrous ether. After

warming for an hour on a steam bath most of the ether was distilled off and one hundred cc. of benzene was added. The mixture was refluxed two hours and was then poured into ice water containing some dilute hydrochloric acid. The benzene layer was removed, washed, and boiled down until the diol began to crystallize from solution. The diol was recrystallized from dilute alcohol using norite. A yield of 3.5 g. of the compound melting at I63° was obtained. Zincke and Tropp report the melting point to be I64°.

9,I0-Dimethylphenanthrene.

A mixture of one gram of the diol in 25 cc. of glacial acetic acid, I0 g. of stannous chloride dihydrate and I0 cc. of concentrated hydrochloric acid was refluxed for one hour. The solution was allowed to cool and then was poured into 500 cc. of slightly acidified water. The suspension settled out overnight and the crude hydrocarbon was filtered, washed and the picrate then made in the usual manner. The picrate (0.7 g.) melted at I92°.

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: C,60.69; H,3.9I.

Found: C,6I.I7; H,4.I5.

Bradsher reports the melting point of the picrate of 9,10-dimethylphenanthrene as 193°-194°(8').

The hydrocarbon was regenerated from the picrate by dissolving the picrate in alcohol, adding dilute ammonium hydroxide and diluting to a volume of 500 cc. The precipitated hydrocarbon was filtered, washed and dried. Upon recrystallization the compound (0.5 g.) formed small white needles which melted at 144°.

Bradsher prepared this hydrocarbon in a different manner and found the melting point to be 142.5°-143°.

9,10-diphenyl-9,10-dihydrophenanthrene-diol

A similar procedure to the preparation of the 9,10-dimethyl-diol was followed. Five grams of the quinone yielded 3 g. of the diol and the melting point checked with that found by Zincke and Tropp.

In the attempt to prepare the 9,10-diphenyl-phenanthrene, a compound was isolated which melted at 198°(uncorr). The melting point of 9,9-diphenyl-10-phenanthrone is reported as 202°.

9,10-diethyl-9,10-dihydrophenanthrene-diol

This compound was prepared in a like fashion to the preceding diols with the exception

the

that glacial acetic acid was used to hydrolyze the Grignard addition product. Also, difficulty was encountered in obtaining this diol in a crystalline form and it has a tendency to remain attached to solvent of crystallization. The diol melted in the range of 116°-120°.

The attempted reduction of the diol was carried out in the presence of stannous chloride and hydrochloric acid. After refluxing for one hour the solution was well cooled in ice to prevent the subsequent formation of an oil upon suspension in 500 cc. of water. It was allowed to stand for two days and then the solid material was collected and washed. The melting point, 64°, is identical with that of 9,9-diethyl-10-phenanthrone as reported in the literature.

9,10-dimethyl-9,10-dihydroanthracene-diol

Three grams of anthraquinone was added slowly to a mixture of 2 g. of magnesium, 11 g. of methyl iodide in a solution of 75 cc. of anhydrous ether and 50 cc. of anhydrous benzene. The reaction mixture was refluxed for six hours. At the end of this time the material was poured into ice water and hydrolyzed

with dilute hydrochloric acid. The material from the benzene-ether layer was recrystallized from benzene. The yield of this diol was 1.2 g. and its melting point, 185°-187°, was within the range reported by Bachmann (9).

9,10-Dimethylanthracene.

The stannous chloride-hydrochloric acid reduction of one gram of 9,10-dimethyl-9,10-dihydroanthracene-diol yielded 0.4 g. of 9,10-dimethylanthracene (m.p. 175°-176°).

2,9,10-Trimethyl-9,10-dihydroanthracene-diol

A small yield of this compound, melting at 145°-150°, was obtained as the hydrolyzed product from the reaction between β-methylanthraquinone and methyl magnesium iodide.

2,9,10-Trimethylanthracene

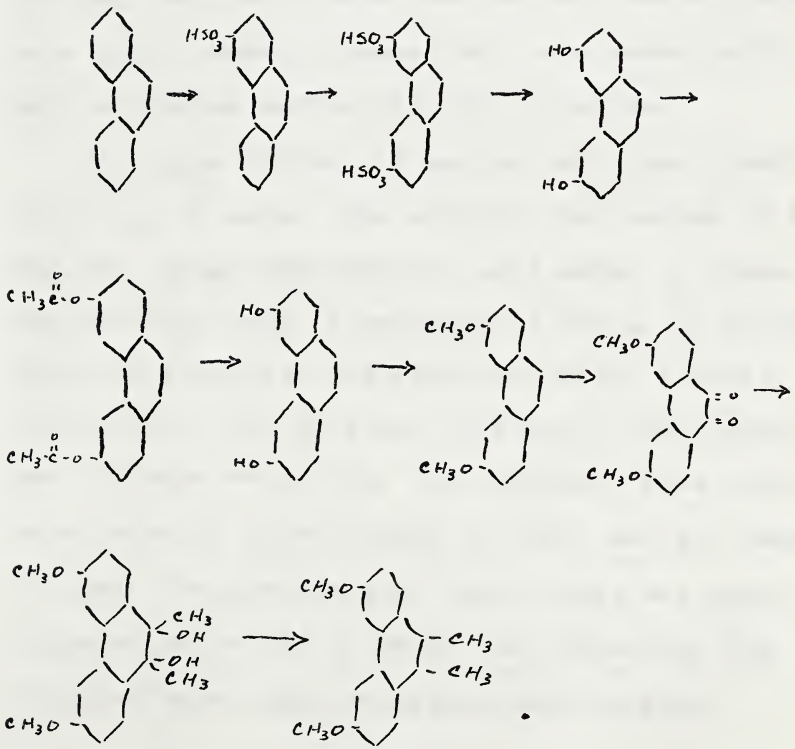
Using a similar procedure and amounts of the same substances 0.7 g. of the diol was converted to the hydrocarbon, the picrate of which, weighed 0.4 g.

The regenerated hydrocarbon (0.2 g.) melted at 96°. Bachmann has found the melting point to be 95°-100°.

The synthesis of

3,6-Dimethoxy-9,10-dimethylphenanthrene

Having established a route for the preparation of 9,10-dimethylphenanthrene from phenanthraquinone, work could now be commenced upon Fieser's synthesis (10) of 3,6-dimethoxyphenanthraquinone starting from phenanthrene. The total synthesis is outlined by the following flow sheet.



Experimental.

To 500 g. of 90% phenanthrene in a 2-l. flask was added 327 cc. of concentrated sulfuric acid. The mixture was heated in an oil bath for four hours at 120°. Constant stirring was maintained during the entire period. The hot solution was then dissolved in 3-4 l. of water and a concentrated solution of 400 g. of sodium hydroxide was added. After thorough cooling the precipitated sodium salt was collected on a large funnel, pressed well and washed with a half saturated sodium chloride solution.

The crude mixture of sodium salts was dissolved in 6-7 l. of water. The solution was heated to boiling and enough hydrochloric acid added to render the solution acid. A solution of 100 g. of barium chloride dihydrate was added and after a short digestion of the barium-2 sulfonate, the mixture was filtered while hot. The filtrate, from which some material crystallized at once, was set aside to cool. The precipitated barium salt was again digested in 6-7 l. of water and collected. The filtered wash water contained only barium-3

sulfonate. The crystallized barium-3 sulfonate from the first filtration was added to the filtrate from the second digestion. The solution was then concentrated to a volume of two litres and a saturated solution of potassium chloride added. This caused the precipitation of the potassium salt of phenanthrene-3 sulfonic acid. The salt was then purified by one recrystallization from water.

One gram of the potassium salt was treated with an excess of p-toluidine and hydrochloric acid. The solution was heated to boiling and enough water added to bring all the material into solution. The melting point of the crystallized material was 215°-218°.

Ninety-four grams of the potassium salt was dissolved in 94 cc. of concentrated sulfuric acid and the mixture was heated and stirred at 125° for one and one-half hours. At the end of this time the mixture was poured into 700 cc. of water and neutralized with a concentrated solution of 200 g. of potassium hydroxide. After slight acidification the solution was boiled down until bumping started. It was then poured into an evaporating dish and dried over an open steam bath.

The finely powdered mixture of disulfonic acids and potassium sulfate was fused with 700 g. of potassium hydroxide at 260°-290°. The melt was dissolved in cold water, partly neutralized, heated and filtered while hot. Hydrochloric acid was then added to the filtrate until the phenanthrols began to form. The mixture was allowed to cool and then filtered. The dried phenanthrol product weighed 50 g. This was dissolved in acetic anhydride and the solution boiled for one hour. It was then poured into water and the diacetates collected. The products were dried over night and the yield obtained was 60 g.

The mixture of diacetates was recrystallized from a small amount of alcohol and then subjected to six fractional recrystallizations from alcohol. Eighteen grams of pure 3,6-diacetoxyphenanthrene was obtained melting at 122°-123°.

The diacetate was hydrolyzed by warming a suspension of the material in alcoholic sodium hydroxide. When the dissolution was complete the solution was diluted with water and slowly acidified at the boiling point. The product (10 g.) was crystallized from a xylene-toluene mixture.

The 3,6-dimethoxyphenanthrene was formed by methylation with alkaline dimethyl sulfate. The ether was crystallized from alcohol and the pure product melted at 102°.

A solution of 8 g. of chromium trioxide was slowly added to 4 g. of the dimethoxy ether dissolved in glacial acetic acid. The temperature of the reaction was kept below 70°. On completion, the solution was well cooled and the collected product washed with alcohol. A single recrystallization from acetic acid gave 1½ g. of the quinone melting at 232° (uncorr).

3,6-Dimethoxy-9,10-dimethyl-9,10-dihydrophenanthrene-diol

The quinone (1½ g.) was finely powdered and slowly added to a Grignard reagent made from 1 g. of magnesium and 5 g. of methyl iodide in 50 cc. of anhydrous ether. The solution was refluxed for one hour and then 50 cc. of benzene was added. After two hours refluxing the cooled solution was poured on to ice water, hydrolyzed with hydrochloric acid and the organic layer was removed and concentrated. The diol (0.6 g.) was found to melt at 115-125°. After two recrystallizations from a benzene-heptane

mixture a crystalline product was obtained which melted at 125°-126°.

For analysis it was dried in vacuo at 80° for three hours. This diol also has a great tendency to remain attached to solvent of crystallization.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0 ; H, 6.7 .
Found : C, 71.4 ; H, 6.9 .

3,6-Dimethoxy-9,10-dimethylphenanthrene.

The diol was dissolved in 25 cc. of acetic acid and 6 g. of stannous chloride and 6 cc. of concentrated hydrochloric acid were added. The solution was refluxed for one hour then cooled and poured into 500 cc. of slightly acidified water. The material was collected, washed and dried.

The crude hydrocarbon was dissolved in alcohol and to the filtered solution at the boiling point was added a filtered solution of picric acid. The picrate (0.4 g.) crystallized out on cooling and the melting point obtained was 186°-187°.

Anal. Calcd. for $C_{24}H_{21}O_9N_3$: C, 58.17; H, 4.27 .
Found : C, 58.33; H, 4.45 .

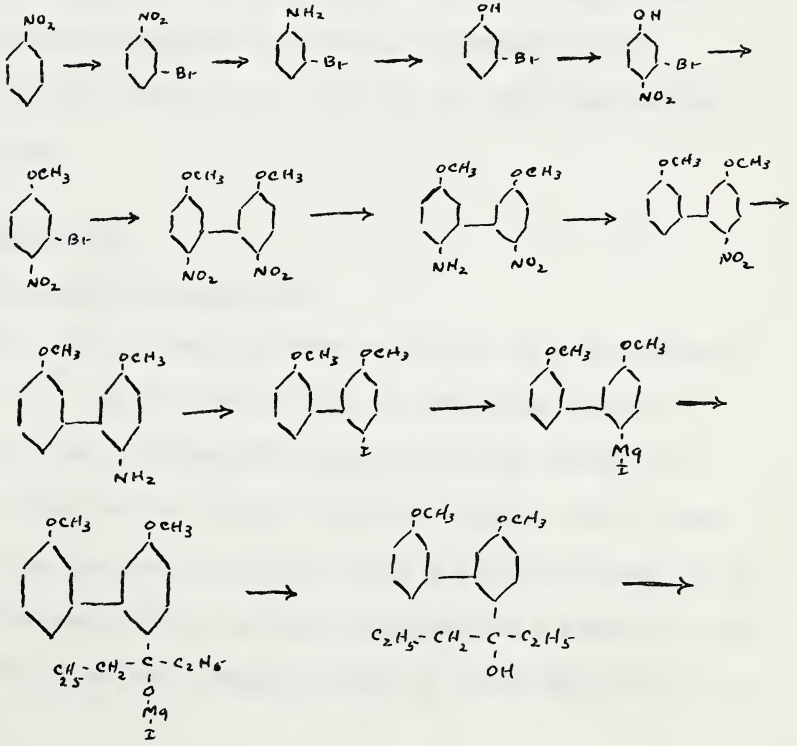
The hydrocarbon was regenerated from the picrate with dilute ammonium hydroxide and after two recrystallizations from alcohol the product weighing 0.25 g. melted at 142°.

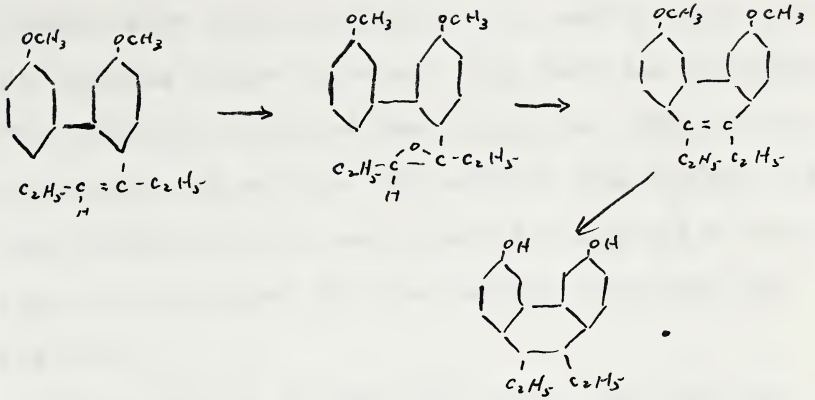
Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2 ; H, 6.8 .
Found : C, 81.1 ; H, 6.8 .

Other Attempts to Prepare 3,6-Dimethoxy-9,10-diethylphenanthrene

The attempts to prepare this compound can be resolved into two main sets of procedures. The first would utilize the aromatic cyclodehydration method established by Bradsher and the second would make use of the reaction with which Kharasch(11) was able to synthesize hexestrol dimethyl ether.

The following flow sheet represents the path followed in the first attempt.





The steps commencing with the interaction of ethyl propyl ketone and the Grignard reagent were taken from Bradsher's general aromatic cyclo-dehydration method and applied to this particular compound.

Experimental.

m-Bromonitrobenzene (12).

Dry, distilled nitrobenzene (123 g.) was placed in a 2-l. flask fitted with a dropping funnel, a stirrer and a Tamworth condenser. The corks were first charred to resist bromine vapors. The flask was then heated in an oil bath at 135°-140° and 26 g. of iron and 255 g. of dry bromine were added in the following manner. Eight grams of iron and 27 cc. of

bromine were mixed and stirred at such a rate that the bromine fumes traversed only half the condenser. This addition required nearly an hour. The mixture was heated and stirred for another hour before the next addition. This was repeated twice and a final 2 g. of iron added and the heating continued for one hour.

The reaction mixture was poured into 500 cc. of water containing 20 cc. of a saturated solution of sodium bisulfite. The contents were then steam distilled, the first portion of which contained a little unchanged nitrobenzene. The yellow crystals of m-bromonitrobenzene were collected on a filter, washed and pressed.

A yield of 110-120 g. of the compound melting at 51° was obtained.

m-Bromoaniline (13).

The nitro compound was reduced to the amine derivative by the action of tin and hydrochloric acid. m-Bromonitrobenzene (203 g.) was added to 360 g. of mossy tin and 700 cc. of water. The mixture was heated to boiling and 500 cc. of concentrated hydrochloric acid was added slowly

at first until the reaction commenced. Refluxing was continued for two hours and then the reaction mixture was cooled and made strongly alkaline with 40% sodium hydroxide solution. The products were then steam distilled and the distillate was extracted with benzene. The benzene extract was dried and then the benzene was distilled off. The crude m-bromoaniline (120-130 g.) was not vacuum distilled.

m-Bromophenol

A mixture of 40 g. of m-bromoaniline, 500 cc. of water and 2½ equivalents of concentrated sulfuric acid was boiled until all the aniline bisulfate had gone into solution. After cooling 100 cc. of sulfuric acid was added to prevent coupling and one equivalent plus a small excess of sodium nitrite was added. The temperature was kept at 0°-5°. To the diazonium salt solution urea was added to destroy any excess nitrous acid and the flask was then heated until bubbles of nitrogen began to evolve. The solution was cooled, the phenol was extracted with benzene and the benzene was washed

and dried over sodium sulfate. Twenty grams of the phenol was distilled at 135-142° (40 mm.).

3-Bromo-4-nitrophenol (14).

In a wide-necked 500 cc. erlenmeyer flask was placed a mixture of 40 g. of concentrated sulfuric acid, 29 g. of sodium nitrate and 70 cc. of water. A solution of 31.6 g. of m-bromophenol in a little alcohol was added drop-wise with constant shaking. The temperature of the reaction was kept below 25°. The contents were allowed to stand for two hours with occasional shaking. Two volumes of water was added and the solid material was washed and steam distilled. The 3-bromo-6-nitrophenol was volatile while the 3-bromo-4-nitrophenol remained in the residue. The residue was extracted four times with boiling water. A yield of 10-12 g. of the phenol melting at 131° was obtained.

3-Bromo-4-nitroanisole (15).

3-Bromo-4-nitrophenol (11 g.) and anhydrous potassium carbonate (10 g.) were finely ground together in a mortar. The solid was then placed in a 250 cc. flask and 25 cc. of xylene and 4 cc. of dimethyl sulfate were added. The material was

refluxed for four hours. After each hour another 4 cc. of dimethyl sulfate was added. The contents were then steam distilled. The xylene passed over first and then the ether. The ether (6-7 g.) melted at 45°.

2,2'-Dinitro-5,5'-dimethoxybiphenyl (16).

Ullmann has outlined the preparation of 2,2'-dinitrobiphenyl and the directions given were applied to this particular compound.

Eleven grams of the ether was heated to 200° in a test tube and 6 g. of powdered copper was added in small amounts with constant stirring. The mass became grey and viscous and at this point the temperature was raised to 220° and kept there for fifteen minutes. The contents of the test tube were cooled, extracted with benzene and refluxed for several minutes. The copper bromide was removed by filtration and the benzene extract was boiled until the biphenyl derivative began to crystallize out. The crude product was crystallized from alcohol using norite and 5 g. of a yellow crystalline

compound melting at 148° was obtained.

Anal. Calcd. for $C_{14}H_{12}O_6N_2$: N_2, 9.2 .

Found : N_2, 9.1 .

2-Nitro-2'-amino-5,5'-dimethoxybiphenyl ? (17).

Purdie has made the 2-nitro-2'-aminobiphenyl from the dinitrobiphenyl using sodium polysulfide in alcohol.

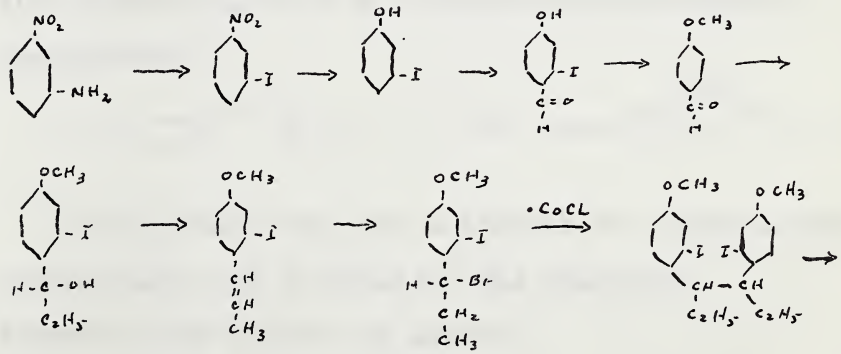
A solution of 100 cc. of ethanol and 9 g. of the dinitrobiphenyl derivative was refluxed with a solution of sodium polysulfide(prepared by boiling 2 g. of sulfur with 8 g. of sodium sulfide crystals and 150 cc. of water until dissolved) slowly added. The solution turned orange and the material was refluxed another two hours and allowed to stand over night. A red-brown solid was obtained which was insoluble in alcohol and benzene. It had no definite melting point and the results from semi-micro nitrogen determinations were inconsistent.

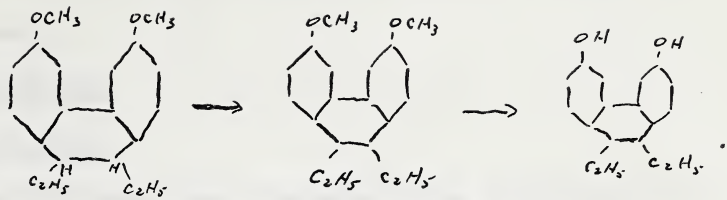
It was then decided that if it were possible to cross an Ullmann reaction between m-iodoanisole and 3-bromo-4-nitroanisole the half-reduction step

could be eliminated. Mixtures of different mole fractions of these compounds were tried but in each case the only substance isolated was the dinitro-dimethoxybiphenyl.

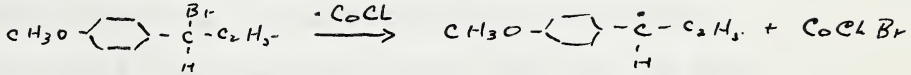
This general method was set aside and work was commenced upon the second set of procedures. This method would involve principally two main reactions. The first necessitates the preparation of o,o'-diiodohexestrol dimethyl ether from m-iodo-anethole hydrobromide and cobaltous subchloride. The second reaction involves an internal Ullmann carried out on o,o'-diiodohexestrol dimethyl ether to give 3,6-dimethoxy-9,10-dihydro-9,10-diethylphenanthrene.

The following flow sheet would then represent the complete synthesis.

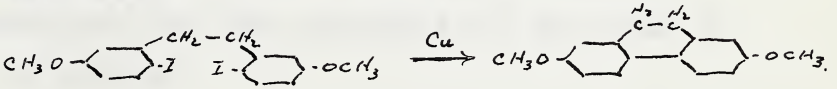




Kharasch and Kleiman (18) have prepared the dimethyl ether of hexestrol from anethole hydrobromide and cobaltous subchloride.



Also, an internal Ullmann reaction has been carried out on 2,2'-diiodo-5,5'-dimethoxybibenzyl (19) converting it to 2,7-dimethoxy-9,10-dihydrophenanthrene.



By applying these two syntheses to m-iodoanethole hydrobromide and by treating the resulting compound with sulfur the desired

3,6-dimethoxy-9,10-diethylphenanthrene might be obtained.

Experimental.

m-Iodophenol

m-Iodophenol was prepared from m-nitroaniline in a series of reactions similar to the preparation of m-bromophenol as reported earlier in this thesis.

2-Iodo-4-hydroxybenzaldehyde (20).

An intimate mixture of 14 g. of slaked lime, 16 g. of sodium carbonate, 8 g. of m-iodophenol, 100 cc. of water and 10 g. of chloroform was heated and shaken until the chloroform layer was seen to disappear. The solution was made acidic and then steam distilled. The 4-iodo-2-hydroxybenzaldehyde passed over in the steam and the 2-iodo-4-hydroxybenzaldehyde remained as a tar in the residue. This was extracted with boiling water and on cooling the material crystallized out. The compound (4 g.) was found to melt at 160°-162°.

2-Iodoanisaldehyde.

Anhydrous potassium carbonate (3.3 g.) and the benzaldehyde derivative (4 g.) were finely ground together and placed in a 250 cc. florence flask. Eight cc. of xylene and 3 cc. of dimethyl sulfate

were added and the mixture was refluxed for several hours. The solution was filtered while hot and on cooling and slow evaporation a very small yield of a compound was obtained melting at 113°.

This synthesis was successful up to this point but was not taken any further since the yields obtained in the Reimer-Tiemann reaction and in the subsequent methylation step were very low . Also, it was now known that phenanthraquinone could be converted to 9,10-dimethylphenanthrene as reported earlier.

Summary

A new method for the preparation of 9,10-dimethylphenanthrenes and 9,10-dialkylanthracenes has been developed. Only 9,10-dimethylphenanthrenes can be made this way since groups larger than methyl groups in the 9,10-phenanthrene-diols migrate in the presence of hydrogen ions to give the substituted phenanthrone. In the case of 9,10-anthracene-diols the groups are further apart and no evidence was found that the hydrogen ion will cause any migration. This procedure can thus be used for the preparation of any 9,10-dialkylanthracene.

The compounds which have been prepared from the corresponding diols by the reduction with stannous chloride and hydrochloric acid include 9,10-dimethylphenanthrene; 9,10-dimethylanthracene; 9,10-diethylanthracene; 2,9,10-trimethylanthracene; 9,10-dimethyl-1,2-benzanthracene; and 9,10-dimethyl-3,6-dimethoxyphenanthrene.

δ^{13}-depleted carbonates.

δ^{18}O-depleted I-P$_2$-bearing rocks; some δ^{18}O-depleted δ^{13}C-depleted carbonates; δ^{13}C-depleted limestones; δ^{13}C-depleted limestones and phosphorites; δ^{18}O-depleted limestones; and phosphorites and phosphatic iron deposits.

The occurrence of iron may have derived from the enrichment of the reduction bulk chemistry of the δ^{13}C-depleted carbonates.

This procedure can then be used for the interpretation of the δ^{13}C-depleted carbonates. In the case of δ^{13}C-depleted carbonates, in the case of δ^{13}C-depleted carbonates, the fossil and the evidence was found that the depletion in δ^{13}C may be due to the presence of δ^{13}C-depleted carbonates, and δ^{13}C-depleted carbonates can be used to interpret the δ^{13}C-depleted carbonates.

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